

THE ABSORPTION SPECTRUM OF BISMUTH SULPHIDE BiS

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(Received for publication, August 24, 1950)

ABSTRACT. Two band systems of the BiS molecule have been obtained in absorption in the near and farther ultraviolet regions ($\lambda\lambda 3056-2351$) and ($\lambda\lambda 2312-2133$). Most of the bands in the two system have been classified, and their vibrational levels assigned. A number of bands, however, remains unclassified of which a list is given in Table II. The band heads seem to fit in the following formulae within experimental error which, in a few cases of weak and diffuse bands, amount to more than 1 \AA , i.e., about 25 wave numbers in the farther ultraviolet region.

$$\text{System I } \gamma = 37217.35 + 378.4 u' - 5.7 u'^2 - 386 u'' + 3.5 u''^2$$

$$\text{System II } \gamma = 45530 + 775 u' - 6.0 u'^2 - 386 u'' + 3.5 u''^2$$

where $u = (v + \frac{1}{2})$.

INTRODUCTION

Sharma (1948) had observed in absorption two prominent band system of the BiSe molecule in the ultra violet regions ($\lambda\lambda 2900-2700$) and ($\lambda\lambda 2350-2200$) respectively at temperatures from 950°C to 1150°C using an absorbing column of vapour of the mixture of bismuth and selenium metals in proportional parts, heated within a graphite tube furnace. It was thought that a similar molecule like BiS of the same group might also give rise to absorption bands near about the same region. Further, there was chemical evidence of the independent and stable existence of BiS molecule with a definite melting point 685°C , which was quite suitable for obtaining an absorbing column of vapour inside the available graphite tube furnace. These considerations led to the present investigation. Two band systems, one very extended and the other much shorter, were obtained in absorption as expected of the molecule in the regions ($\lambda\lambda 3056-2351$) and ($\lambda\lambda 2312-2133$) which were degraded to the red and to the violet end respectively. The heads of nearly all the bands of the extended system seem to fit in the formula,

$$\text{I } \gamma = 37217.35 + 378.4 u' - 5.7 u'^2 - 386 u'' + 3.5 u''^2$$

and those fewer band heads of the shorter system fit in the formula

$$\text{II } \gamma = 45530 + 775 u' - 6.0 u'^2 - 386 u'' + 3.5 u''^2$$

The agreement between the observed and calculated values of the band heads of the first system, particularly for higher values of v' , is not satisfactory in view of the fact that proper assignment of v' values for a case like this is not possible, as discussed later. The constants for the system II are not quite

certain on account of very insufficient number of bands. The formula proposed is, however, the best approach possible to explain the position of the band heads observed.

EXPERIMENTAL

A pure specimen of the Bi_2S_3 molecule could not be obtained, and hence a sample of the salt was prepared by passing H_2S in a BiCl_3 solution. The precipitate was washed several times repeatedly until it was definitely established by chemical tests that it became free from hydrochloric acid. The precipitate was left for several days inside a desiccator. The salt so prepared was introduced into a vitreosil tube, about 5 mm bore and 20 cms long, which was inserted into the Acheson graphite tube of a vacuum furnace. The furnace was originally designed and used by Saha, Sur and Mazumdar (1926) for their work on thermal ionisation and later on modified and used in this laboratory by many workers for experiments on absorption spectra. The graphite tube was held in a horizontal position by means of carbon blocks fixed to the electrodes with nuts and bolts. The electrodes, as well as the walls of the furnace, were kept cool by a water circulating arrangement. The projecting ends of the furnace in the lengthwise direction were closed by quartz windows which were cemented by sealing wax. The line joining the centres of the windows was adjusted to coincide with the axis of the hollow graphite tube. The furnace was provided with side windows to make observation inside the furnace. The electrodes were heated electrically by a heavy current of several amperes derived from the secondary of a step down 10 k.w. transformer operated by 110 volts-A.C. The graphite tube could be heated to a temperature of about 2000°C by inductive control in the primary circuit of the transformer.

The source of continuum was a water cooled hydrogen discharge tube fitted with a quartz window. The discharge was run by a 3-k.w., H.T. transformer operated by 110 volts-A.C. The spectrum was photographed with a copper comparison spectrum on B.20 Kodak plates with a medium sized quartz spectrograph. An optical pyrometer was used for measuring the temperature of the furnace. An exposure ranging from 45 minutes to 1 hour 20 minutes was necessary to bring out the bands on the plates.

Both the systems of absorption bands develop within 850°C – 1000°C which seems to be the optimum range for observing these bands. Three different exposures are taken at temperatures $(850-875)^\circ\text{C}$, $(925-950)^\circ\text{C}$ and $(950-1025)^\circ\text{C}$. A progressive development of bands was observed. In the first plate was recorded only 25 bands. In the second, additional bands $\lambda_{2980.5}$, $\lambda_{2732.7}$, $\lambda_{2569.7}$, $\lambda_{2554.8}$, $\lambda_{2516.7}$, $\lambda_{2498.8}$, $\lambda_{2481.2}$, $\lambda_{2435.7}$, $\lambda_{2418.8}$, $\lambda_{2406.7}$ and $\lambda_{2392.3}$ were recorded, and in the third a number of additional bands were developed, though very weak, towards the ν' progression, as analysis has revealed. The following additional bands were observed on the third spectrogram: $\lambda_{3055.8}$, $\lambda_{2560.9}$, $\lambda_{2477.2}$, λ_{2470} , $\lambda_{2464.5}$, $\lambda_{2453.9}$; $\lambda_{2451.3}$, $\lambda_{2447.3}$, $\lambda_{2433.3}$, $\lambda_{2392.3}$, $\lambda_{2377.3}$, $\lambda_{2357.8}$, $\lambda_{2351.6}$.

SYSTEM I

TABLE I

λ in Å	Int. in absorption	γ obs. in cms^{-1}	γ cal cms^{-1}	Analysis ν' , ν''
3055.8	3	32715	32713	2, 16
3044.8	1	32833	32832	0, 13
3024.6	3	33053	33057	3, 16
3017.9	2	33126	33127	0, 12
2999.2	3	33333	33331	3, 15
2990.5	3	33430	33429	0, 11
2980.5	2	33542	33556	2, 13
2954.0	3	33843	33851	1, 12
2961.2 ?	5	33760	33758	0, 10
2927.4	6	34150	34152	2, 11
2921.4	3	34220	34232	4, 13
2888.3	4	34612	34607	8, 16
*2861.5	5	34937	
2825.9	6	35377	35388	0, 5
2800.4 ?	0	35698	35674	11, 15
2797.2	10	35740	35739	0, 4
2769.5	10	36097	36097	0, 3
2741.8	7	36462	36462	0, 2
2713.9	6	36836	36834	0, 1
2687.1	9	37204	37201	1, 1
2663.3	10	37536	37529	3, 2
2638.0	9	37896	37901	3, 1
2615.1	9	38230	38234	4, 1
2593.1	8	38553	38555	5, 1
2554.1 ?	0	39143	39164	7, 1
2517.2	2	39247	39244	6, 0
2528.2	4	39542	39543	7, 0
2516.7	1	39723	39727	9, 1
2509.3	1	39810	39830	8, 0
2507.2	3	39873	39872	11, 2

TABLE I (contd.)

λ in \AA	Int. in absorption	γ obs. in cm^{-1}	γ cal in cm^{-1}	Analysis ν' , ν''
2498.8	1	40607	39991	10, 1
2491.7	0	40121	40114	12, 2
2477.2	1	40356	40344	13, 2
2470 ?	2	40461	40474	12, 1
2464.5	1	40564	40563	14, 2
2451.3	0	40783	40770	15, 2
2447.3	1	40849	40865	12, 0
2433.3	1	41084	41094	13, 0
2418.8	2	41330	41324	18, 2
2406.7		41538	41523	17, 1
2392.3	0	41788	41775	21, 2
2377.3	0	42052	42075	18, 0
2357.8	0	42399	42391	23, 1
2351.6	0	42511	42496	24, 1

? Position of the head uncertain

TABLE II

List of unclassified bands (Taken from all the plates)

λ in \AA	Intensities
* 2857.0	3
2829.5	0
2732.7	2
2576.2	2
2571.5	1
2560.7	1
2560.9	0
2551.5	0
2481.2	2
2453.0	0
2435.7	0
2338.9	2
2316.4	4
2282.7	0

* Marked completely in the O II bands of the continuum, measurement of the head absolutely uncertain.
 o Not visible under comparator, visual estimate.

System II

TABLE III

λ in Å	Intensities	γ obs cms ⁻¹	γ cal cms ⁻¹	Analysis ν' ν''	
2312.2	4	43235	43218	0	7
2296.2	9	43537	43555	0	6
2277.2	10	43900	43890	0	5
2258.4	8	44265	44250	0	4
2222.9	4	44972	44973	0	2
2204.7	8	45343	45345	0	1
2186.4	8	45723	45724	0	0
2168.5	8	46100	46108	1	1
2150.1	4	46495	46487	1	0
2133.4	2	46859	46859	2	1

TABLE IV

The few band heads observed in system II can be arranged in the following scheme :

ν'	2	46859						
	1	46495	46100					
	0	45724	45343	44972	44608	44265	43900	43537 43235
	$\nu'' \rightarrow$	0	1	2	3	4	5	6 7

TABLE V

24	42511																	
23	42399																	
22																		
21			41788															
20																		
19																		
18	42052		41330															
17		41538																
16																		
15			40782															
14			40564															
13	41084		40356															
12	40849	40461	40121														35698	
11			39873															
10		40007																
9		39727																
8	39840																34612	
7	39543																	
6	39244																	
5		38553																
4		38230																
3		37896	37536														33333	33053
2																	32715	
1		37204																
0		36836	36462	36097	35740	35377				33760	33430	33126	32847					
ν'	ν''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Deslander's Scheme

Some of the bands which came out on the 2nd plate were found missing on the 3rd plate taken at a higher temperature. These are $\lambda_{2857.0}$ and $\lambda_{2569.7}$ which fall in the list of unclassified bands as appended in Table II.

RESULTS

In making out the final list of band heads of the BiS molecule, the best possible mean of the measurements from the different plates are taken wherever the bands are observed on more than one plate. Table I gives the wave lengths in \AA in air, visual estimates of their intensities on the scale of 10, wave numbers observed in cm^{-1} in vacuum and those calculated from the formula. The last column gives the vibrational analysis.

Table V gives the Deslandre's scheme for system I, Fig 1 gives the intensity plots of the band heads and the Frank Condon parabola, Table III and Table IV give the corresponding arrangements for system II.

Table II gives the list of unclassified bands which are all of very poor intensity. The position of their heads are mostly uncertain, and they are observed in any one plate.

General features of transitions in absorption for system I, as depicted in Table V, can be explained by the upper and lower states *A* & *B*, as shown in Fig. 2 in which $r_e' > r_e''$, $\omega' < \omega''$ and D_0' slightly less than D_0'' . Table V shows that bands $v'', 0$ and $v', 0$ to 5 are not observed, which is explained by the above figure. The thin continuous lines, shown vertically from v'' to v' levels of the electronic states *B* and *A* respectively, serve to explain the

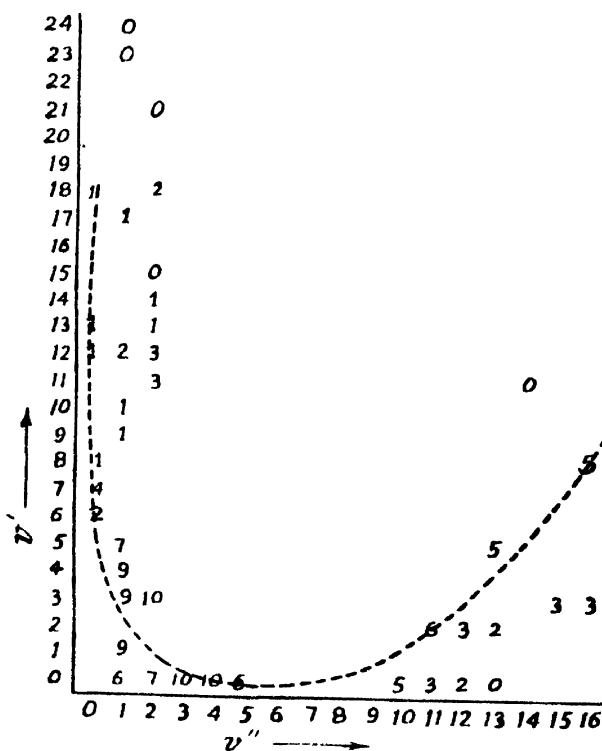


FIG. 1

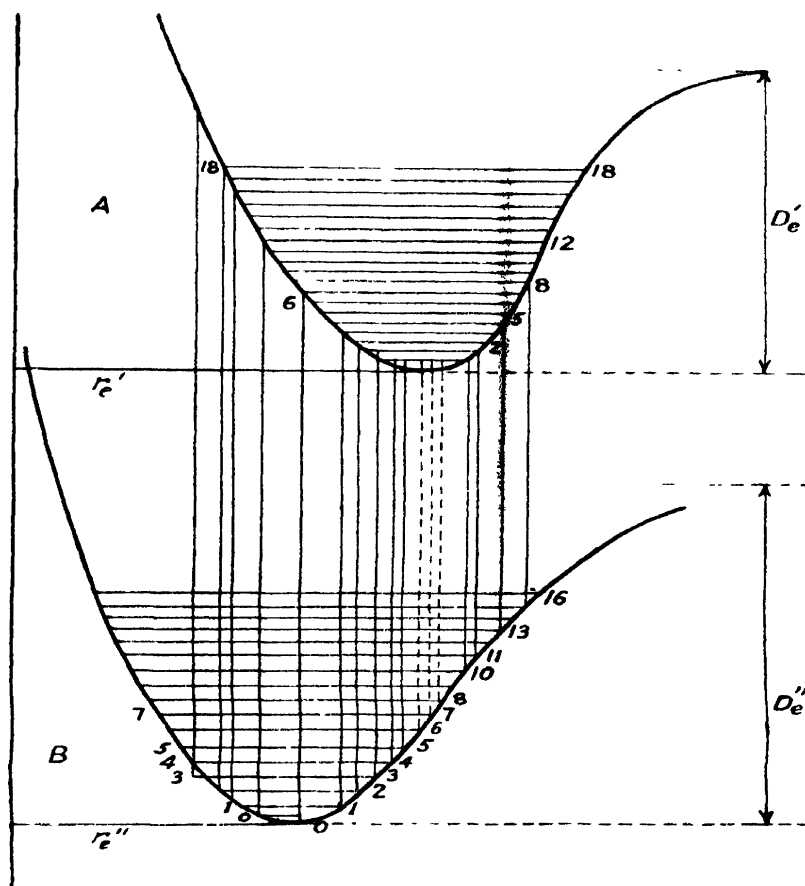


FIG. 2

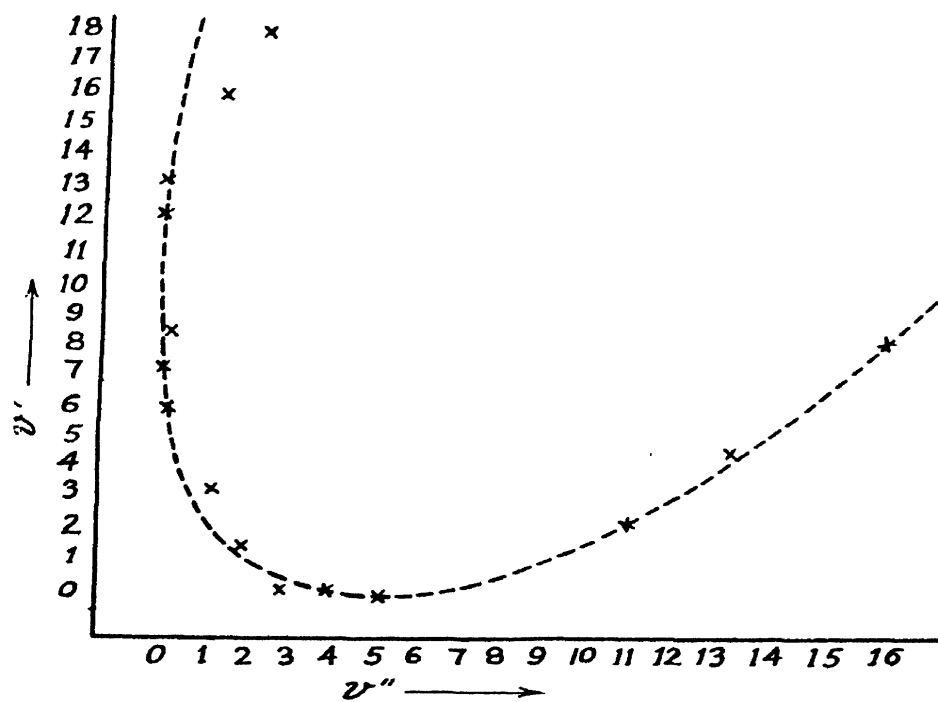


FIG. 3

observed bands of strong and moderately strong intensities according to Frank and Condon principle. The figure explains that transitions from the r_{\min} side of v'' levels 3, 4 and 5 are not possible so that bands with v'' equal to 3, 4 and 5 to $v', 0$ are only possible from r_{\max} side of these v'' levels as are actually observed, and shown in Table V.

Transition indicated by thin dotted lines are either inadmissible or else have poor intensities, as they end on about the middle of the 0-0 level of the upper state A where the kinetic energy of oscillation of the level is greatest. This possibly explains why in Table V no bands are observed for $v', 0$ and $v'', 6$ to 9.

For a typical case as this where $r_e' > r_e''$, $\omega' < \omega''$ and D_0' slightly less than D_0'' , u_r curves are asymmetrical about r_e , i.e., equilibrium positions and molecules spend an extended period of stay at the r_{\max} positions, so that transitions from r_{\max} positions of the μ_r curves are more probable.*

Intensities, as expected in absorption from the ground state B to the upper state A according to Frank and Condon principle, are shown in figure 3. The expected Frank Condon parabola shows the asymmetrical branches along the v' and v'' progression with the intensities along v'' more pronounced. All these facts are in agreement with the observed intensity plots of the bands and the Frank Condon parabola as shown in Fig. 1. Only strong transitions according to Frank-Condon principle are considered in obtaining this curve from the two states A and B of Fig. 2.

* Type IV discussed on page 39 in Introduction to Molecular Spectra by R. C. Johnson (Methuen).

ACKNOWLEDGMENT

The author is grateful to Dr. K. Mazumdar, D.Sc. for his interest and guidance in this investigation.

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